DEVELOPMENT AND CHARACTERIZATION OF 3D-PRINTABLE PLA FILAMENTS REINFORCED WITH FISH SCALE POWDER IN ADDITIVE MANUFACTURING PROCESSES

A SYNOPSIS

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1. INTRODUCTION

The advent of Industrial 4.0 has indicated a transformative era in manufacturing, characterized by the integration of automation and cutting-edge technologies. 3D printing, leveraging CAD, enhances the efficiency and precision of product fabrication [1]. As an important role in additive manufacturing, 3D printing offers reduced waste, faster production, and design versatility, with Fused Deposition Modeling (FDM) notable for its accessibility and cost-effectiveness [2]. The push for sustainable manufacturing has led to increased use of waste-derived materials in 3D printing, providing ecological and economic gains [3]. With the marine industry's significant seafood waste, including fish scales, utilizing these byproducts in composite development aligns with circular economy goals. Reusing and recycling such materials can transform them into bio-based inputs for products like biopolymers, contributing to environmental preservation and value creation within the seafood processing industry. Researchers are exploring ways to integrate these bio-fillers into polymers to improve composite performance [4]. Polylactic acid (PLA) is a prominent material in FDM-based 3D printing, valued for its biodegradability, biocompatibility, and cost-effectiveness. Efforts to refine PLA's properties through additives and print settings are advancing, with enhancements in tensile strength and material robustness observed with the addition of carbon or jute [5]. The precise control of infill density, layer thickness, and nozzle temperature is crucial for optimizing the strength and quality of 3D prints, guiding research towards high-strength component production [6].

This study aims to advance sustainable additive manufacturing by exploring the use of fish scale waste as a bio-filler in PLA filaments and fine-tuning 3D printing parameters for improved mechanical outcomes [7]. As sustainability becomes a paramount goal, additive manufacturing is uniquely positioned to convert waste into high-value products, reinforcing a circular economy and reducing environmental footprints [8]. This research, through cross-disciplinary efforts and innovation, explores the frontiers of sustainable additive manufacturing, envisioning a synergy between ecological responsibility and manufacturing progress. The adoption of waste-derived materials in additive manufacturing marks a significant shift towards more sustainable material uses and

innovative production techniques. It not only achieves resource and cost efficiency but also plays a vital role in reducing the industry's ecological impact. This approach is pivotal for advancing a circular economy and promoting environmental sustainability within the manufacturing sector [9]. Additionally, the use of bio-fillers like fish scales enhances the mechanical attributes of printed items, driving the development of stronger, more durable, and sustainable composites. This convergence of waste utilization and materials science innovation is crucial for expanding the potential of additive manufacturing and tackling environmental issues [10]. Integrating waste-derived bio-fillers in additive manufacturing enhances not just mechanical properties but also contributes to natural resource conservation and waste reduction. This strategy prevents waste from reaching landfills, aligning manufacturing with environmental sustainability and resource conservation efforts [11]. Additionally, optimizing 3D printing parameters is crucial for the quality and performance of components. Fine-tuning settings such as infill density and layer thickness improve part strength and production efficiency, promoting innovation in additive manufacturing [12]. Interdisciplinary research is key in advancing sustainable additive manufacturing. Collaboration across sectors can drive innovation, bridging gaps between research, application, and policy, fostering a supportive ecosystem for sustainable practices [13]. Finally, the combination of material innovation with process optimization covers the way for additive manufacturing to be a beacon of sustainable industry, offering a balance of economic, environmental, and social benefits [14].

2. LITERATURE REVIEW

Slapnik et al. [15] Incorporating core-shell rubber (CSR) into polylactic acid (PLA) has been evaluated for enhancing the mechanical and thermal properties essential for 3D printing applications. This hybrid material's performance has been rigorously tested through a series of assessments, including bending, Charpy impact, dynamic mechanical analysis (DMA), and tensile tests. The addition of 10wt% CSR to PLA significantly improves flexural modulus and impact resistance. Specifically, the injection molding process boosts Charpy impact strength by an impressive 746%, while the 3D printing approach records a 109% increase. The PLA-CSR blend maintains, and in some instances, amplifies the flexural strength when compared to pure PLA. The mechanical robustness of

PLA filament containing CSR surpasses that of standard ABS filament. Relative to pure PLA, the PLA-CSR fusion has shown an 18% upsurge in impact resistance. The integration of Glycidyl Methacrylate (GMA) with CSR substantially elevates the toughness of PLA. Notably, introducing a 10wt% combination of GMA and CSR enhances the PLA's elongation at break to 449%, achieving a substantial improvement over the baseline PLA. The resilience of the PLA combined with GMA and CSR also shows a remarkable increase, attaining an energy absorption capacity of 130.71MJ/m3, which is markedly higher than that of pure PLA. The stability issues and processing challenges associated with Wooden Plastic Composite (WPC) filaments have been addressed by substituting PLA with CSR detritus and the incorporation of an acrylic processing aid (APA) prior to filament production.

Liao et al. [16] The study of Polylactic Acid (PLA) combined with Acetylated Tannin (AT) composites focuses on examining key mechanical properties such as elongation, tensile strength, and Young's modulus. It has been observed that the incorporation of 20% AT into PLA does not compromise the tensile integrity of the resultant composite. For optimal 3D printing outcomes, it is recommended to maintain processing temperatures below 250°C to ensure the material's stability. The PLA-AT blend has demonstrated its efficacy as a filament for 3D printing, effectively mitigating common issues like phase separation and the accumulation of acetylated tannin, provided the extrusion is conducted at temperatures below 220°C.

Xiao et al. [17] This study explores the performance of Polylactic Acid (PLA) when blended with bio-filler hemp hurd to create a filament suitable for both Fused Deposition Modeling (FDM) and Injection Molding (IM) processes. The research assesses the composite's flexural, tensile, and impact strength. Findings indicate that PLA combined with Hemp Hurd (HH) enhances the flexural modulus for both FDM printed and IM parts. FDM printing in particular has been shown to deliver superior impact strength and more precise dimensional accuracy compared to IM. The surface texture analysis, supported by Scanning Electron Microscope (SEM) imagery, revealed that an increase in HH concentration correlates with greater surface roughness and a more pronounced corrugated texture. There is a noted distinction between FDM printed parts and those created through IM, emphasizing the importance of the mechanical analysis and the process-structure

relationship for the IM technique. The FDM approach is thus highlighted as advantageous for industrial applications. The study also evaluated the effects of ageing on composite materials, noting a decrease in Young's Modulus, flexural modulus, tensile strength, flexural strength, and fracture toughness, while impact strength increased in both untreated and alkali-treated hemp fiber composites. Notably, the mechanical properties showed marked improvement with the alkali-treated hemp fibers.

Pickering and Aruan Efendy [18] Surface treatment of hemp fibers significantly boosts the interfacial shear strength in composite materials made from both Polylactic Acid (PLA) and unsaturated polyester. The inclusion of a mix of hemp and lyocell fibers into nonwoven polylactide composites also leads to enhancements in mechanical properties when compared to composites reinforced with a single type of material. These hybrid composites exhibit improved tensile and flexural strength, desirable Young's modulus, reduced density, and low water absorption rates. The investigation delves into Fused Deposition Modeling (FDM) for fabricating filaments from PLA combined with hemp and harakeke (a type of flax). It evaluates the influence of 10, 20, and 30 wt% harakeke and hemp on the tensile and Young's moduli of the printed samples. The study reveals that adding hemp and harakeke to PLA generally increases the tensile modulus of the material. The integration of a plasticizer aids in improving layer adhesion and the quality of the surface finish while reducing the porosity of the composite. The fiber orientation within the composites plays a crucial role in their mechanical performance, with this study achieving maximum fiber orientation factors (Kθ) of 0.44 for hemp and 0.58 for harakeke. In terms of tensile strength, the harakeke and hemp composites attained values of up to 101.6MPa and 87.3MPa, respectively. These strengths are significantly higher than that of pure PLA, with increases of 90% and 60%, showcasing the substantial potential of these bio-fiber reinforced composites for enhanced material properties in FDM applications.

Ozyhar et al. [19] the study investigates the impact of varying wood filler content on the characteristics of Polylactic Acid (PLA) filaments for Fused Deposition Modeling (FDM) 3D printing. Six different proportions of wood content, ranging from 0 to 50%, were tested. As the wood content in the filament increased, there was a notable decrease in filament density. Interestingly, with the addition of 10% wood particles, the tensile strength of the filaments showed a slight improvement, increasing from 55MPa to 57MPa.

However, further increasing the wood content to 50% resulted in a significant reduction in tensile strength, bringing it down to 30MPa. The study also notes that pure PLA components had a smooth surface finish without voids, while the addition of wood particles led to a rougher and more porous surface texture with visible wood clusters. Additionally, the torsional storage modulus of the 3D printed parts was found to diminish with the incorporation of wood particles. Without wood additives, PLA remains a standard commercial filament. However, the research highlighted that a functionalized polymer acted as an effective bonding agent within the PLA/wood composites. The findings also indicate that layer thickness plays a crucial role in influencing surface roughness and wettability in 3D printed PLA/wood composites. The study found that wood particle absorption and temperature effects can adversely affect the performance of PLA-based Wood-Plastic Composites (WPC) under hydrothermal conditions. The application of alkenyl succinic anhydride (ASA) on treated minerals was observed to reduce the viscosity of the molten polymer, aiding in flow control during processing. To ensure sufficient interfacial adhesion and optimal composite characteristics, it is essential to process the PLA-based WPC at temperatures significantly above the melting point of PLA, which involves extrusion, injection, and compression techniques.

Aggarwal et al. [20] this research evaluates the effects of integrating diatomaceous earth (DE) into polylactic acid (PLA) filaments for 3D printing. While bio-based PLA filaments have been advantageous in reducing the costs associated with 3D printing, this study examines whether the addition of diatomaceous earth impacts the overall cost-effectiveness by altering filament properties. The study reveals that incorporating DE into PLA filaments results in a decline in their mechanical properties. Specifically, the inclusion of 5wt% diatomaceous earth led to a 19% reduction in the yield point, and with a 10wt% addition, the yield point saw a further 3% reduction. When the DE content was increased to 15wt%, a significant deterioration in all the properties was observed, with the exception of Young's modulus. Contrary to the decreases seen in other mechanical characteristics, the research notes an increase in Young's modulus and yield stress values following the addition of diatomaceous earth to the PLA. This finding suggests that while the diatomaceous earth may contribute to stiffer filaments, it also makes them more prone to yielding under stress. The investigation into PLA-DE filaments highlights the complexity

of balancing improvements in certain properties with potential compromises in others.

Battegazzore et al. [21] this study examines the enhancement of mechanical properties in 3D printed parts made from PLA filaments reinforced with carbon fibers and talc using Fused Deposition Modeling (FDM). The research indicates that pure PLA typically exhibits weaker interlayer bonding and a higher degree of mechanical anisotropy compared to other polymer composites. The introduction of talc and carbon fibers into PLA filaments was found to significantly improve these characteristics due to a reduction in melt viscosity. The addition of talc, in particular, demonstrated a dual role by reinforcing and toughening the PLA matrix. The improvement is attributed to the effective interfacial bonding achieved between PLA and talc, as well as the alignment of the talc particles during the manufacturing process. While adding fillers generally led to a reduction in flexural strength, the study found that PLA with 3% talc and PLA with 6% talc exhibited increases in flexural strength, reaching 3555MPa and 3566MPa, respectively, which is a noticeable improvement over unfilled PLA. The study also highlights that the composite formulation and the crystallization temperatures exert a substantial influence on the crystallization behavior of PLA/talc composites during the cooling phase. The incorporation of talc into PLA not only enhances the polymer's crystallization rate but also contributes efficiently to the overall improved performance of PLA-based 3D printed materials.

Magalhães da Silva et al. [22] in this study, the properties of biodegradable filaments made from Cork and Polylactic Acid (PLA) for use in Fused Deposition Modeling (FDM) were explored. The research found that as cork content was increased, there was a corresponding decrease in tensile strength and an increase in impact strength. Furthermore, higher percentages of cork resulted in lower composite density, with an improvement in specific strength and specific tensile strength attributes. To mitigate the inherent brittleness of PLA, Tributyl Citrate (TBC), a biodegradable plasticizer, was utilized. The introduction of TBC led to a decrease in Young's modulus and tensile strength, but it notably increased the ductility of the composites, making the material more pliable and less likely to break under stress. The addition of cork as a filler was found to be compatible with filament production for FDM applications. The resultant Cork-Polymer Composites (CPC) filaments were suitable for 3D printing, creating objects with unique properties. These

included a non-plastic feel, a warm tactile experience, a natural color, and the emission of a pleasant cork odor during the printing process. However, the study also notes that increasing cork content may compromise mechanical properties. Therefore, it suggests a maximum addition of 5% cork to maintain a balance between enhanced ductility and adequate mechanical strength, ensuring the functionality and structural integrity of 3D printed objects.

2. OBJECTIVES

1. Characterize the Physical and Chemical Properties of 3D Printable Filaments:
   Conduct comprehensive analyses including XRD, FTIR, TGA, tensile tests, and SEM to evaluate the structural integrity, chemical stability, and mechanical properties of PLA-fish scale composite filaments.
2. Characterize the Mechanical and Morphological Properties of 3D Printed Composite Specimens:
   Evaluate composite specimens through tensile, flexural, impact, hardness tests, and water absorption tests to determine their suitability for durable, real-world applications.
3. Optimize 3D Printing Process Parameters Using Taguchi Methods:
   Utilize the L16 orthogonal array matrix to systematically adjust and optimize infill patterns, densities, layer thickness, and nozzle temperature, aiming to enhance the material properties and print quality of the composites.

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4. RESEARCH PROBLEMS

1. Evaluate the feasibility of utilizing fish scale waste as a reinforcement material in PLA filaments for 3D printing, considering its abundance and potential as an eco-friendly alternative to traditional reinforcement sources.
2. Investigate the impact of incorporating fish scale powder (FSP) into PLA filaments on mechanical properties such as tensile strength, flexural strength, impact resistance, and hardness, aiming to identify potential improvements compared to neat PLA filaments.
3. Assess the printability of PLA/FSP filaments by examining parameters such as

diameter deviation, surface roughness, and uniformity of FSP distribution within the filaments. Optimize the fused deposition-based 3D printing parameters, including infill patterns, infill density, layer thickness, and nozzle temperature, to achieve optimal printing quality and mechanical performance.

4. Analyze the sustainability aspects of PLA/FSP filaments compared to conventional PLA filaments, considering factors such as resource utilization, waste reduction, energy consumption, and biodegradability. Determine the environmental benefits and drawbacks associated with using fish scale waste as a reinforcement material in 3D printing applications.
5. Explore potential applications of PLA/FSP bio-composite filaments in various industries, such as biomedical, automotive, and construction, based on their enhanced mechanical properties and sustainability profile. Assess the economic viability of large-scale production and commercialization of PLA/FSP filaments, considering factors such as cost-effectiveness, market demand, and regulatory compliance.

5. ORGANIZATION OF THESIS

Chapter 1: Introduction

This chapter sets the stage for the study by presenting the context and rationale behind the research. It introduces the concept of 3D printing, the significance of biodegradable polymers like PLA, and the innovative use of fish scale powder as a reinforcing agent. The chapter outlines the research gaps, objectives, and potential contributions to the field of additive manufacturing, emphasizing the move towards sustainable practices.

Chapter 2: Literature Review

The literature review provides a comprehensive examination of existing studies related to PLA composites, the role of natural fillers in enhancing material properties, and the specific application of bio-fillers in 3D printing. It critically evaluates previous findings on mechanical, thermal, and surface characteristics of reinforced filaments, establishing the foundation for the current study.

Chapter 3: Materials and Experimental Methods

This chapter describes the methodology, beginning with the procurement and preparation of materials, detailing the formulation of PLA and fish scale powder composites. It covers the experimental setup for 3D printing, the specific tests performed for material characterization, and the techniques used for analyzing mechanical and thermal properties, as well as SEM analysis.

Chapter 4: Results and Discussion

Results obtained from tensile, flexural, and impact tests, TGA, water absorption studies, and SEM are presented and thoroughly discussed in this chapter. The performance of each composite is evaluated against established benchmarks, with a focus on understanding the influence of fish scale powder content on the observed behaviors.

Chapter 5: Conclusions

The final chapter synthesizes the findings, drawing conclusions about the effects of fish scale reinforcement on PLA filaments. It addresses the research objectives, discusses the implications for the additive manufacturing industry, and suggests areas for future work. The chapter concludes by highlighting the study's contribution to sustainable material development in 3D printing.

6. RESULTS AND DISCUSSION

a. Characterization of PLA/FSP composite filaments

Figure 1 offers a comprehensive graphical depiction of the process for producing filaments reinforced with fish scale powder (FSP) for use in 3D printing. It begins with cutla fish, which are processed to extract the scales. These scales are then ground into a fine powder and mixed with PLA pellets to create a composite material. This material is fed into a twin-screw extruder, as shown in the schematic, where it is melted and formed into a continuous filament suitable for 3D printing. Below the extrusion process diagram, the figure provides microscopic and topographical analyses of the extruded filaments, highlighting the microstructure and surface roughness across various FSP concentrations (0%, 10%, 20%, 30% by weight).

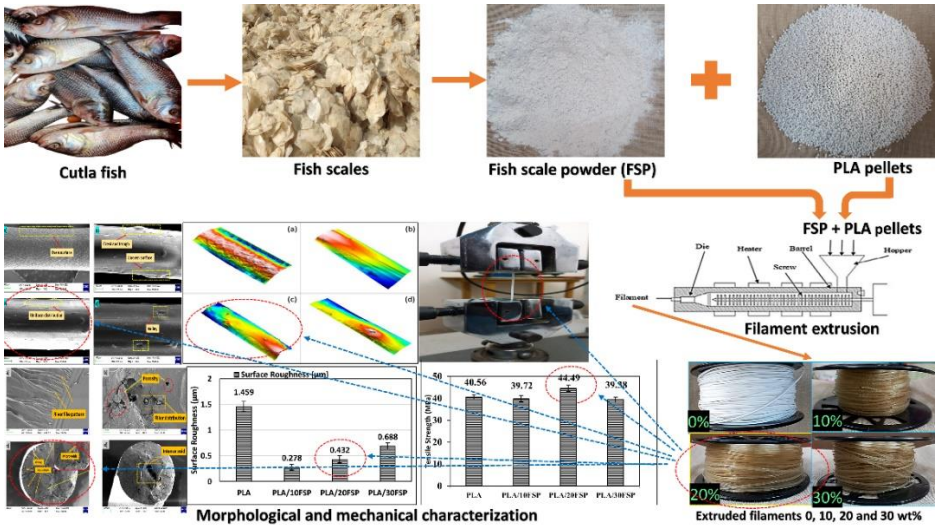

Figure 1. Graphical illustration of PLA-reinforced FSP filament fabrication using a twin-screw extruder.

Figure 2 illustrates the tensile strength results for PLA filaments reinforced with varying percentages of fish scale particles. Pure PLA filaments showed a tensile strength and modulus of 40.56 MPa and 2.5 GPa, respectively. However, the introduction of 20 wt% fish scale particles into the filaments significantly increased their tensile strength and modulus to 44.49 MPa and 2.83 GPa. This improvement is linked to the even distribution of fish scales, which efficiently transfer the load to the PLA matrix, enhancing the composite's overall tensile properties. Conversely, adding 10 wt% fish scales resulted in a decrease in tensile strength and modulus due to surface irregularities and filler distribution issues. Furthermore, filaments with 30 wt% fish scale particles saw a decline in tensile properties, likely due to reduced polymer viscosity and particle aggregation. Optimizing the filler content is crucial to balance reinforcement and maintain the composite's mechanical integrity.

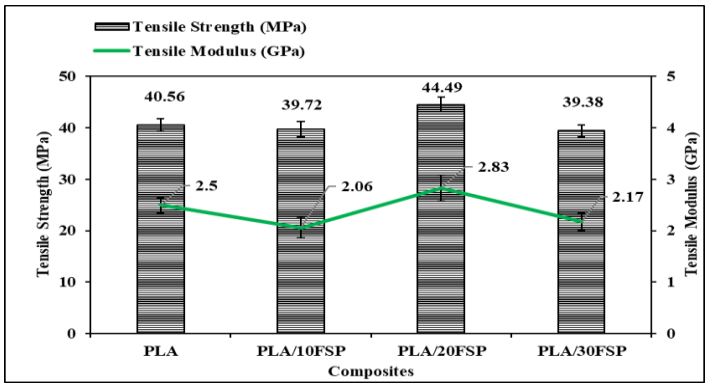

Figure 2. Filament tensile parameters of PLA/FSP composites

As a result, the formation of voids within the filament becomes restricted, serving as focal points for stress that lead to the spread of cracks and ultimately, early failure. The addition of bio-fillers at concentrations of 0, 10, and 20 wt% led to increments in elongation at break by 10.02, 10.41, and 10.75%, respectively. However, incorporating 30 wt% fish scale particles resulted in a reduction of the elongation percentage by 10.55%, as depicted in Figure 3. This trend underscores a significant improvement in tensile strength across samples with different filler levels.

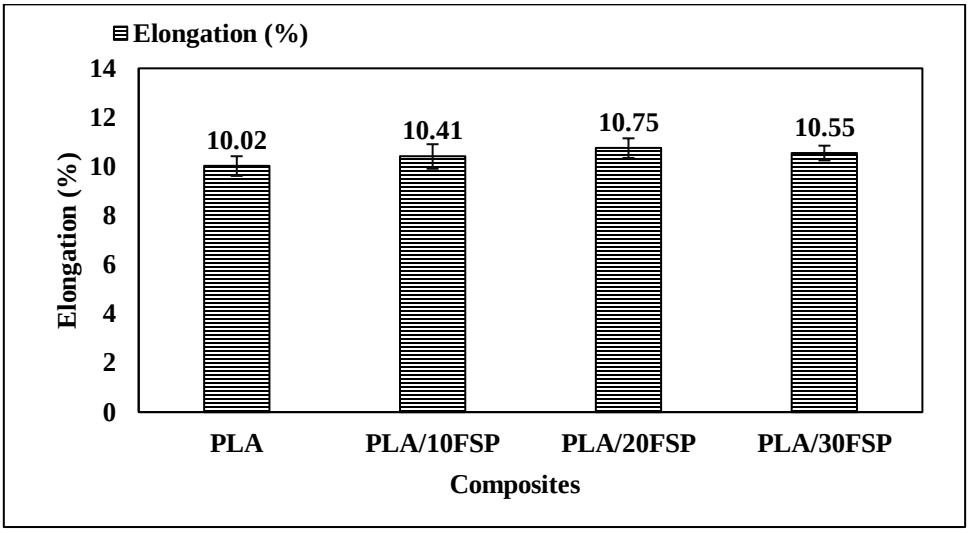

Figure 3. Filament elongation of PLA/FSP composites

Figure 4 demonstrates the variations in the diameter of fish scale-reinforced PLA filaments. The diameter deviation notably increases for composites containing 20 wt% fish scale particles. A minor deviation of -0.002 mm was recorded with the addition of 10 wt% fish scale particles to the PLA, indicating minimal impact on viscosity and maintaining smoothness in filament structure. However, with concentrations exceeding 10 wt%, there's a noticeable shift towards larger deviations. Specifically, filaments with 30 wt% fish scale content showed a significant decrease in diameter, deviating by -0.006 mm, suggesting that the diameter exceeded the optimal 1.75 mm mark. This effect, characterized by the presence of irregularities like peaks and troughs, reflects the complex interplay between the amount of filler and the extrusion process. The increase in filler leads to challenges in maintaining a consistent filament diameter due to dispersion difficulties, indicating a critical point beyond which additional filler reduces uniformity. This pattern underscores the importance of rheological properties in determining the quality of the extruded filament, highlighting the need for further research to fine-tune the balance

between filler content and filament consistency in PLA/FSP composites.

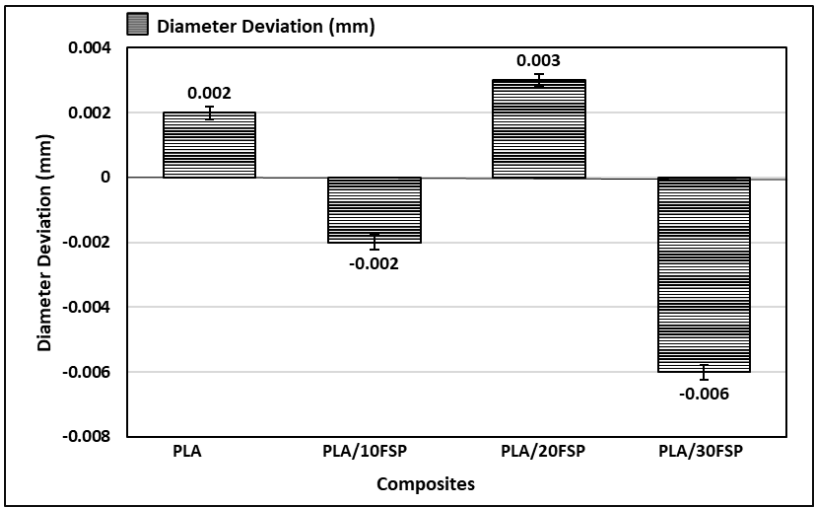

Figure 4. Diameter deviation of the PLA/FSP composites

Figure 5 showcases the effect of fish scale particle inclusion on the surface roughness of PLA filaments. Initial findings indicate that the base PLA filament exhibits a surface roughness of 1.459 µm, the highest among the samples tested. With the introduction of fish scale particles, surface roughness values were recorded at 0.278 µm, 0.432 µm, and 0.688 µm for 10%, 20%, and 30% fish scale compositions, respectively. The composite with 10% fish scale particles showed the smoothest surface at 0.278 µm, suggesting that the presence of these particles at lower concentrations contributes to a finer filament surface. This reduction in roughness at lower fish scale levels could be due to better particle dispersion and stronger interfacial adhesion, leading to smoother filament surfaces. Conversely, an increase in particle content beyond this point hints at possible particle clustering or distribution issues, detracting from the surface smoothness. Such variations highlight the delicate balance between filler quantity and the resulting surface characteristics in composite filaments, reflecting the complex dynamics of filler integration in polymer matrices. The graphical representations from Figure 5 (a-d) further illustrate this trend, with pure PLA showing greater surface disparities, underscoring the impact of fish scale incorporation on filament surface topography.

Figure 6 presents SEM images showcasing the cross-sectional views of PLA filaments with varying concentrations of fish scale reinforcements. The SEM visuals reveal that pure PLA filaments display smooth, consistent cross-sections devoid of any surface irregularities or fractures. Through Figures 7 (a–d), highlighting 0%, 10%, 20%, and 30%

fish scale additions, it's observed that fish scale particles are evenly dispersed across the filament matrixes, with the 20% reinforcement showing particularly uniform particle

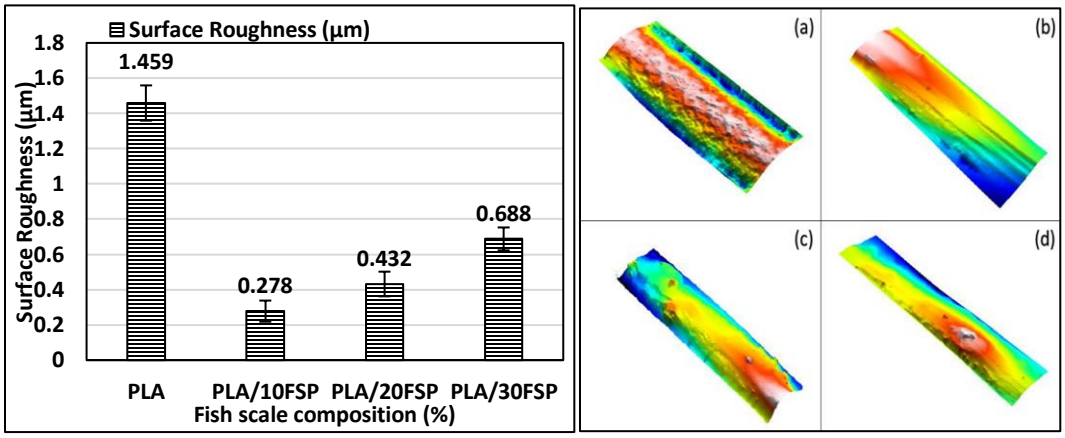

Figure 5. Surface roughness value of the PLA/FSP compositions and 3D surface roughness plot of (a) neat PLA (b) PLA/FSP10% (c) PLA/FSP20% (d) PLA/FSP30%

distribution. At up to 20% reinforcement, the filaments begin to exhibit slight textural variations along their edges. Conversely, Figure 8's SEM images of the 30% fish scale-reinforced PLA filaments uncover pronounced textural anomalies such as peaks and troughs, indicative of voids and surface defects. These patterns mirror the effects seen in research by Mohamad Bayat et al., which explored the impact of incorporating silicon particles into PLA filaments, suggesting a commonality in the behavior of particulate fillers within a PLA matrix.

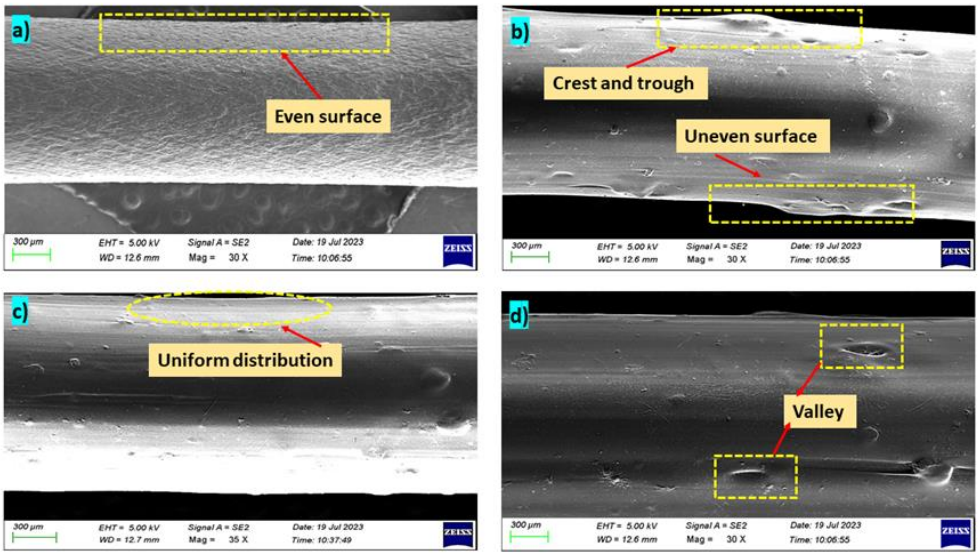

Figure 6. SEM of the extruded PLA/FSP reinforced filaments (a) neat PLA (b) PLA/FSP10% (c) PLA/FSP20% (d) PLA/FSP30%

Figure 7 shows SEM images capturing the fracture patterns of PLA/FSP bio composite filaments. In the image marked as 8 (a), a neat PLA filament fracture is shown, characterized by a distinctive river-like pattern on its cross-section, suggesting a typical brittle fracture. The image in 8 (b) reveals the presence of porosity and a rough fracture surface in composites containing 10 wt% filler, where filler materials are evenly distributed throughout the composite. Image 8 (c) depicts the fracture surface of 20 wt% reinforced filaments, highlighting the presence of voids and deformation patterns such as kinking, alongside initial material flaws, echoing observations from similar studies. Lastly, 8 (d) vividly shows the fracture surface of filaments with 30 wt% filler, marked by pronounced voids, a finding that corroborates with insights from prior research, indicating a trend towards increased structural anomalies with higher filler content.

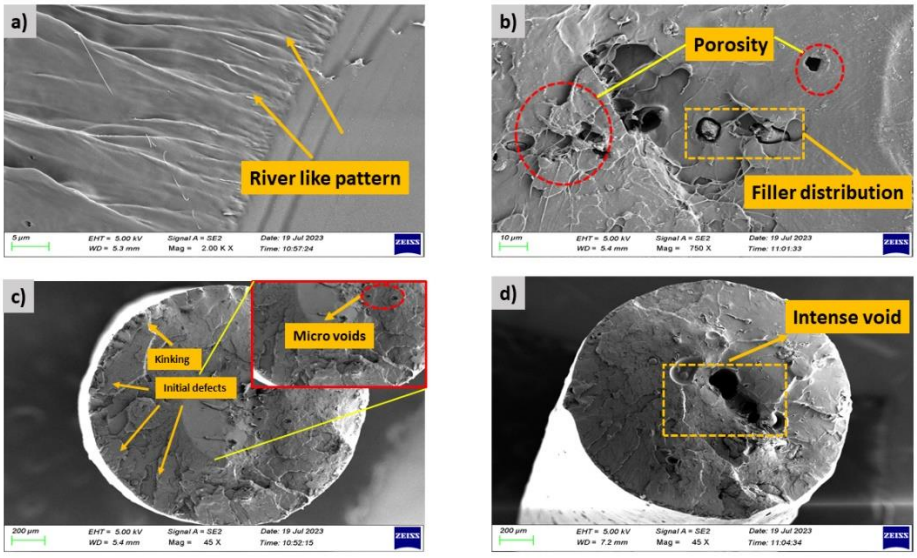

Figure 7. Tensile fracture of PLA/FSP composite filaments (a) neat PLA (b) PLA/FSP10% (c) PLA/FSP20% (d) PLA/FSP30%

This study explored the use of repurposed fish scale particles to reinforce PLA filaments for 3D printing, aiming to produce biocompatible components. The optimal addition of 20 wt% fish scale to PLA resulted in filaments with the highest tensile strength of 44.49 MPa, demonstrating improved mechanical properties. However, higher fish scale contents increased surface roughness and diameter variation, affecting the print quality. The research indicates that fish scale bio-fillers are promising for sustainable 3D printing, combining ecological benefits with advanced material performance. The 20 wt% PLA-fish scale blend emerged as ideal for biocompatible products, setting the stage for further

studies into bio-polymeric filaments enhanced with recycled materials.

b. Characterization of PLA/FSP composite specimens

Figure 8 presents a detailed graphical abstract illustrating the creation of PLA/FSP composite specimens for 3D printing. Starting with cuttlefish, the process involves harvesting and pulverizing fish scales into a fine powder. This powder is then blended with PLA pellets, forming the basis of the composite material. The blend is subsequently processed in a twin-screw extruder, depicted in the schematic, where it is melted and extruded to produce a continuous filament. Below the figure provides microscopic and topographical analyses of the composite specimens, highlighting the mechanical characterization across various FSP concentrations (0%, 10%, 20%, 30% by weight).

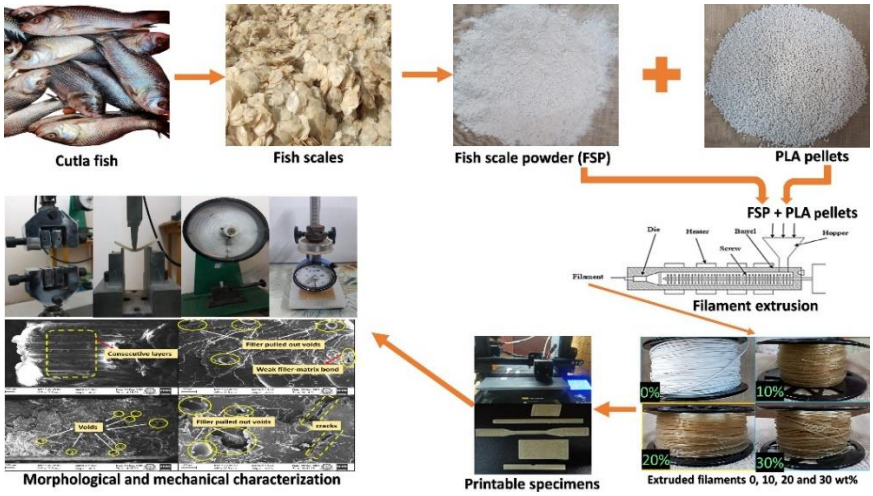

Figure 8. Graphical abstract for PLA/FSP composite specimens

Figures 9 and 10 display the impact of incorporating fish scale powder into PLA on tensile properties such as strength, modulus, and elongation at break. The data indicate that the baseline tensile strength for pure PLA composites stands at 35 ± 1.2 MPa. Enhancing the PLA matrix with 20 wt% fish scale powder significantly boosts tensile strength over composites with 10% and 30% filler concentrations. Specifically, PLA composites with 20% fish scale powder (FSP) exhibit superior tensile modulus compared to the neat PLA, with measurements for 10%, 20%, and 30% FSP loadings at 2.06 ± 0.1, 3.23 ± 0.2, and 2.17 ± 0.1 GPa, respectively. This increase is linked to the introduction of high-stiffness micron-sized additives, creating more rigid structures within the composite matrix. Elongation at

break sees enhancements of 17.28%, 19%, and 19% for 10%, 20%, and 30% bio-filler concentrations, respectively, demonstrating improved flexibility with the addition of fish scale powder.

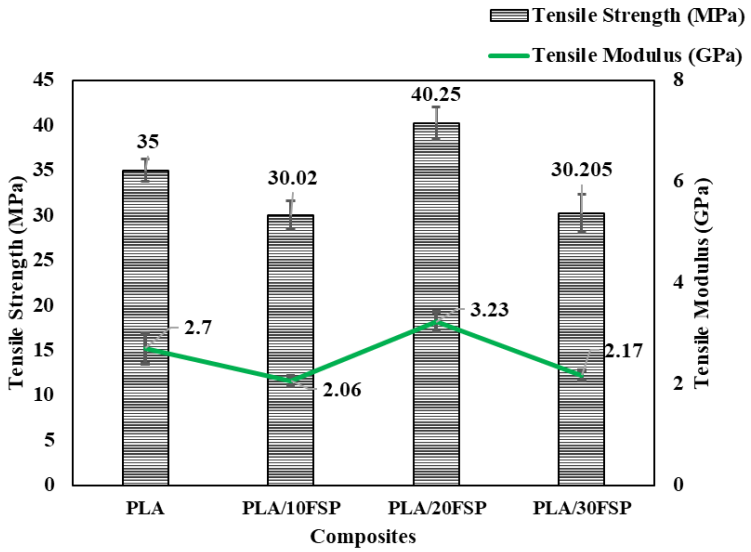

Figure 9. Tensile Strength and Modulus of PLA/FSP composites.

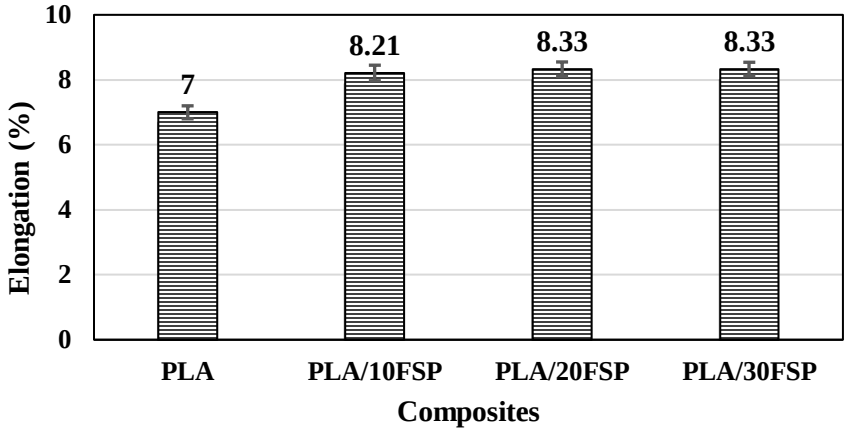

Figure 10. Elongation at Break of PLA/FSP composites.

The evaluation of the flexural properties of the developed composites was carried out through a 3-point bending test, as depicted in Figure 11. The investigation highlights that the inclusion of fish scale powder (FSP) notably enhances the flexural strength of the PLA/FSP20 composite. For the PLA/FSP0 sample, the flexural strength was recorded at 588.42 ± 1.4 MPa. Upon integrating fish scale powder into the PLA matrix, the flexural strength for PLA/FSP10, PLA/FSP20, and PLA/FSP30 composites were measured at

460.15 ± 1.6 MPa, 822.53 ± 1.8 MPa, and 420.833 ± 2 MPa, respectively, showcasing a significant improvement for the PLA/FSP20 composite. This composite demonstrated the highest flexural strength of 822.53 ± 1.8 MPa among the samples, underlining the positive impact of 20 wt% fish scale particle inclusion on the composite's bending performance. The enhancement in flexural strength with fish scale particles indicates the effective contribution of these inorganic fillers to the mechanical reinforcement of the PLA composite.

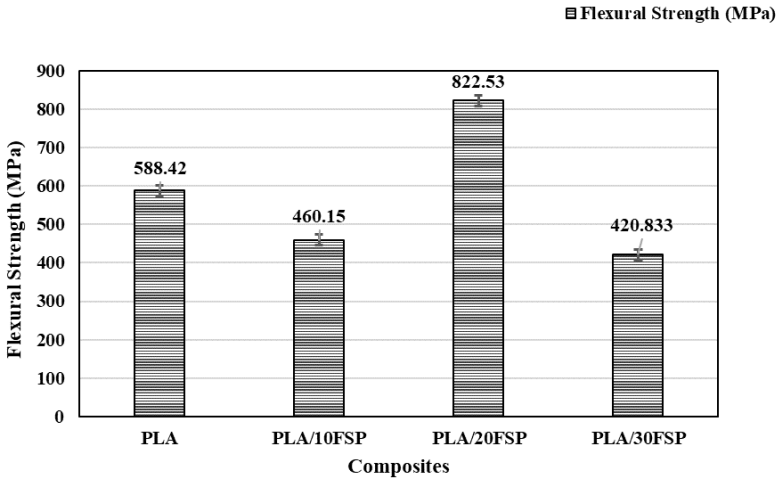

Figure 11. Flexural strength of PLA/FSP composites.

Impact strength values were observed at 0.2 J for pure PLA, 0.12 J with 10% fish scale particle incorporation, 0.25 J at 20% concentration, and 0.14 J with 30% fish scale particles in the PLA matrix, as outlined in Figure 12. The inclusion of fish scale powder at a concentration of 20 wt% resulted in the printed specimens exhibiting superior impact resistance. This enhancement in the ability to absorb and withstand impacts in polymeric composites is due to the dissipation of energy in the damaged area and the redirection of the fracture path away from the rigid filler particles.

Hardness assessments conducted on the composites, as depicted in Figure 13, revealed that introducing fish scale particles into the PLA matrix resulted in an increase in hardness, ranging from 34.45 to 39.793 HV. Notably, the inclusion of 20 wt% fish scale powder into the PLA led to a 15.5% enhancement in hardness, reaching a peak of 39.793 HV. This increase in hardness is attributed to the rigid nature of fish scale powder, which bolsters the composite's resistance against localized plastic deformation from indentation, thereby contributing to a higher hardness value.

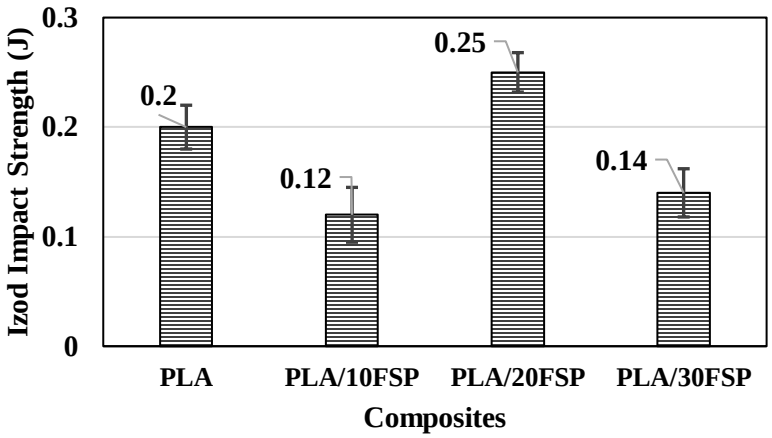

Figure 12. Impact properties of PLA/FSP composites

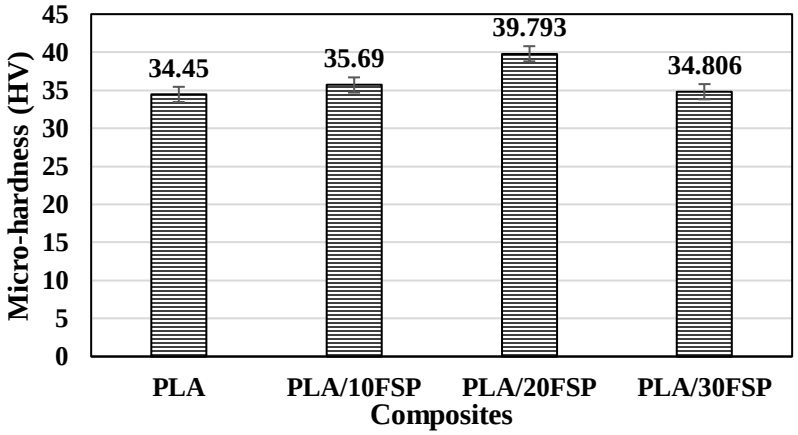

Figure 13. Hardness values of the PLA/FSP composites

Scanning electron microscope (SEM) images capturing the fractured surfaces of 3D printed tensile specimens with varying filler volumes (0%, 10%, 20%, and 30%) are presented in Figure 14. These images illustrate the filaments and how voids between layers are filled in the 3D printed samples. Failures in the material occur due to filament breakage, filler detachment, and inadequate layer adhesion, leading to the formation of voids and cracks.

Utilizing fish scale waste as an enhancement for extruding PLA filaments for 3D printing has led to the development of environmentally friendly materials. Incorporation of fish scale particles into PLA filament production has yielded significant findings:

- ✓ Composite filaments with 20% fish scale particle content demonstrated superior tensile strength, reaching 40.25±1.8 MPa, and underwent comprehensive mechanical property evaluation, showing enhanced flexural strength at this specific fish scale

concentration within PLA-based composites.

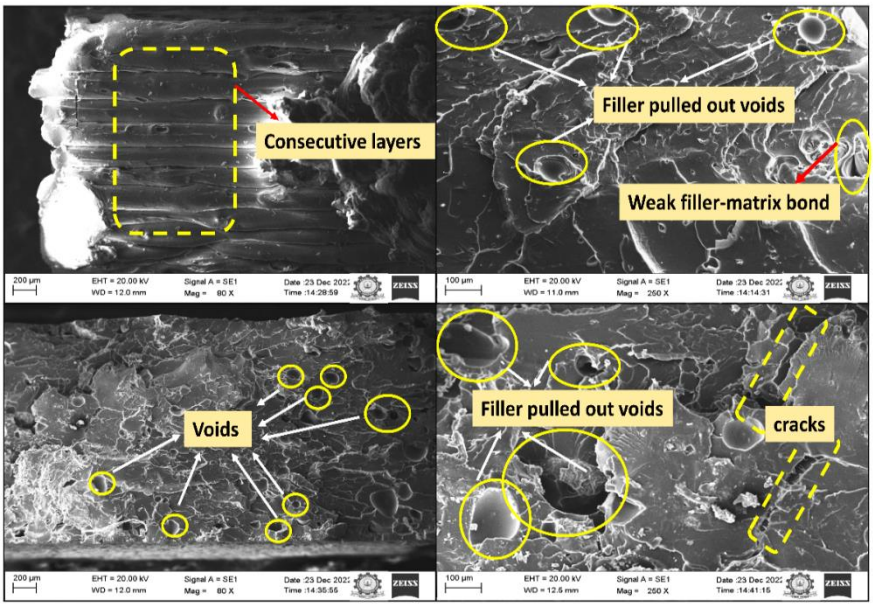

Figure 14. SEM micrographs of tensile fractured samples

- ✓ The inclusion of fish scale particles at this concentration also appeared to boost the impact resistance of the PLA composites, with the peak impact strength recorded at 0.25 J. This improvement is likely attributable to the fish scales' contribution to the composite's overall toughness and its enhanced capability to dissipate energy from sudden impacts more efficiently than the base PLA matrix.
- ✓ Filaments containing 20% fish scale powder showed increased hardness compared to other compositions and demonstrated the lowest rate of water absorption, with only 1.05% observed, indicating superior physical properties among the specimens tested.
- ✓ The mechanical performance of the PLA/FSP (20%) composites surpassed that of the unenhanced PLA. SEM analysis of the tensile-tested PLA/FSP composite revealed a distinctive morphology characterized by voids, cracks, and the interaction between the filler and the PLA matrix, in contrast to the smoother appearance of the standard PLA composite.
- ✓ These outcomes suggest that filaments augmented with fish scale powder, particularly at a 20% inclusion rate, present a viable option for fabricating materials with enhanced mechanical properties for Fused Deposition Modeling (FDM) 3D printing technologies.

7. REFERENCES

[1] M. Mehrpouya, A. Dehghanghadikolaei, B. Fotovvati, A. Vosooghnia, S. S. Emamian, and A. Gisario, The Potential of Additive Manufacturing in the Smart Factory Industrial 4.0: A Review, *Applied Sciences* **9** (2019), 3865.

[2] A. F. Ahmad Zamri, N. Ayn Ahmad Sayuti, A. H. Ab Hamid, and M. A. A. Mohd Noor, Additive Manufacturing-3D Printing in Product Design Education: Learning experiences using Fused Deposition Modeling (FDM), *Environment-Behaviour Proceedings Journal* **7** (2022), 511–516.

[3] C. Xu, M. Nasrollahzadeh, M. Selva, Z. Issaabadi, and R. Luque, Waste-to-wealth: biowaste valorization into valuable bio(nano)materials, *Chemical Society Reviews* **48** (2019), 4791–4822.

[4] R. Phiri, S. Mavinkere Rangappa, S. Siengchin, O. P. Oladijo, and H. N. Dhakal, Development of sustainable biopolymer-based composites for lightweight applications from agricultural waste biomass: A review, *Advanced Industrial and Engineering Polymer Research* **6** (2023), 436–450.

[5] R. Mandala, A. P. Bannoth, S. Akella, V.K. Rangari, and D. Kodali, A short review on fused deposition modeling 3D printing of bio-based polymer nanocomposites, *Journal of Applied Polymer Science* **139** (2021).

[6] K. Dwivedi, S. Joshi, R. Nair, M. S. Sapre, and V. Jatti, Optimizing 3D printed diamond lattice structure and investigating the influence of process parameters on their mechanical integrity using nature-inspired machine learning algorithms, *Materials Today Communications* **38** (2024), 108233.

[7] C. S. Wu, S. S. Wang, D. Y. Wu, and W. L. Shih, Novel composite 3D-printed filament made from fish scale-derived hydroxyapatite, eggshell and polylactic acid via a fused fabrication approach, *Additive Manufacturing* **46** (2021), 102169.

[8] A. Kassab, D. Al Nabhani, P. Mohanty, C. Pannier, G. Y. and Ayoub, Advancing Plastic Recycling: Challenges and Opportunities in the Integration of 3D Printing and Distributed Recycling for a Circular Economy, *Polymers* **15** (2023), 3881.

[9] Nwakamma Ninduwezuor-Ehiobu, Olawe Alaba Tula, Chibuike Daraojimba, Kelechi Anthony Ofonagoro, Oluwaseun Ayo Ogunjobi, Joachim Osheyor Gidiagba, et al., Exploring Innovative Material Integration in Modern Manufacturing for Advancing U.S.

Competitiveness in Sustainable Global Economy, *Engineering Science & Technology Journal* **4** (2023), 140–168.

[10] P. C. Srinivasa, and R. N. Tharanathan, Chitin/Chitosan — Safe, Ecofriendly Packaging Materials with Multiple Potential Uses, *Food Reviews International* **23** (2007), 53–72.

[11] A. M. King, S. C. Burgess, W. Ijomah, and C. A. McMahon, Reducing waste: repair, recondition, remanufacture or recycle?, *Sustainable Development* **14** (2005), 257–267.

[12] A. M. E. Arefin, N. R. Khatri, N. Kulkarni, and P. F. Egan, Polymer 3D Printing Review: Materials, Process, and Design Strategies for Medical Applications, *Polymers* **13** (2021), 1499.

[13] E. B. Reynolds, and Y. Uygun, Strengthening advanced manufacturing innovation ecosystems: The case of Massachusetts, *Technological Forecasting and Social Change* **136** (2018), 178–191.

[14] J. Costa, and J. C. O. Matias, Open Innovation 4.0 as an Enhancer of Sustainable Innovation Ecosystems, Sustainability **12** (2020), 8112.

[15] J. Slapnik, R. Bobovnik, M. Mešl, and S. Bolka, Modified Polylactide Filaments for 3D Printing with Improved Mechanical Properties, *Contemporary Materials* **7** (2016).

[16] J. Liao, N. Brosse, A. Pizzi, S. Hoppe, X. Zhou, G. Du, Characterization and 3D printability of poly (lactic acid)/acetylated tannin composites, *Ind. Crops Prod.* 149 (2020): 112320.

[17] X. Xiao, V.S. Chevali, P. Song, D. He, H. Wang, Polylactide/hemp hurd biocomposites as sustainable 3D printing feedstock, *Compos. Sci. Technol*. **184** (2019), 107887.

[18] K.L. Pickering, M.G. Aruan Efendy, Preparation and mechanical properties of novel bio-composite made of dynamically sheet formed discontinuous harakeke and hemp fibre mat reinforced PLA composites for structural applications, *Ind. Crops Prod.* **84** (2016), 139–150.

[19] T. Ozyhar, F. Baradel, J. Zoppe, Effect of functional mineral additive on processability and material properties of wood-fiber reinforced poly(lactic acid) (PLA) composites, *Compos. Part A Appl. Sci. Manuf.* **132** (2020), 105827.

[20] S. Aggarwal, S. Johnson, D. Saloni, M. Hakovirta, Novel 3D printing filament

composite using diatomaceous earth and polylactic acid for materials properties and cost improvement, *Compos. Part B Eng.* **177** (2019), 107310.

[21] D. Battegazzore, S. Bocchini, and A. Frache, Crystallization kinetics of poly (lactic acid)-talc composites, *Express Polymer Letters* **5** (2011), 849–858.

[22] S. P. Magalhães da Silva, T. Antunes, M. E. V. Costa, and J. M. Oliveira, Cork-like filaments for Additive Manufacturing, *Additive Manufacturing* **34** (2020), 101229.

3. LIST OF PUBLICATIONS

[1] **A. Joseph Arockiam**, S. Rajesh, and S. Karthikeyan, Development of fish scale particle reinforced PLA filaments for 3D printing applications, *Journal of Applied Polymer Science* **141** (2023).

[2] **A. Joseph Arockiam**, S. Rajesh, S. Karthikeyan, Senthil Muthu Kumar Thiagamani, R. G. Padmanabhan, Mohamed Hashem, Hassan Fouad, and AbuZar Ansari, Mechanical and thermal characterization of additive manufactured fish scale powder reinforced PLA biocomposites, *Materials Research Express* **10** (2023), 075504.

[3] **A. Joseph Arockiam,** S. Rajesh, S. Karthikeyan, and G. B. Sathishkumar. "Optimization of fused deposition 3D printing parameters using taguchi methodology to maximize the strength performance of fish scale powder reinforced PLA filaments." *International Journal on Interactive Design and Manufacturing* (IJIDeM) (2024): 1-14.